On Rates and Mechanisms of OH and O_3 Reactions with Isoprene-derived Hydroxy Nitrates

Supporting Information

Lance Lee[1], Alex P. Teng[2], Paul O. Wennberg[2], John D. Crounse[2] and Ronald C. Cohen**[1,3]*

1. Department of Chemistry at University of California, Berkeley CA 94709

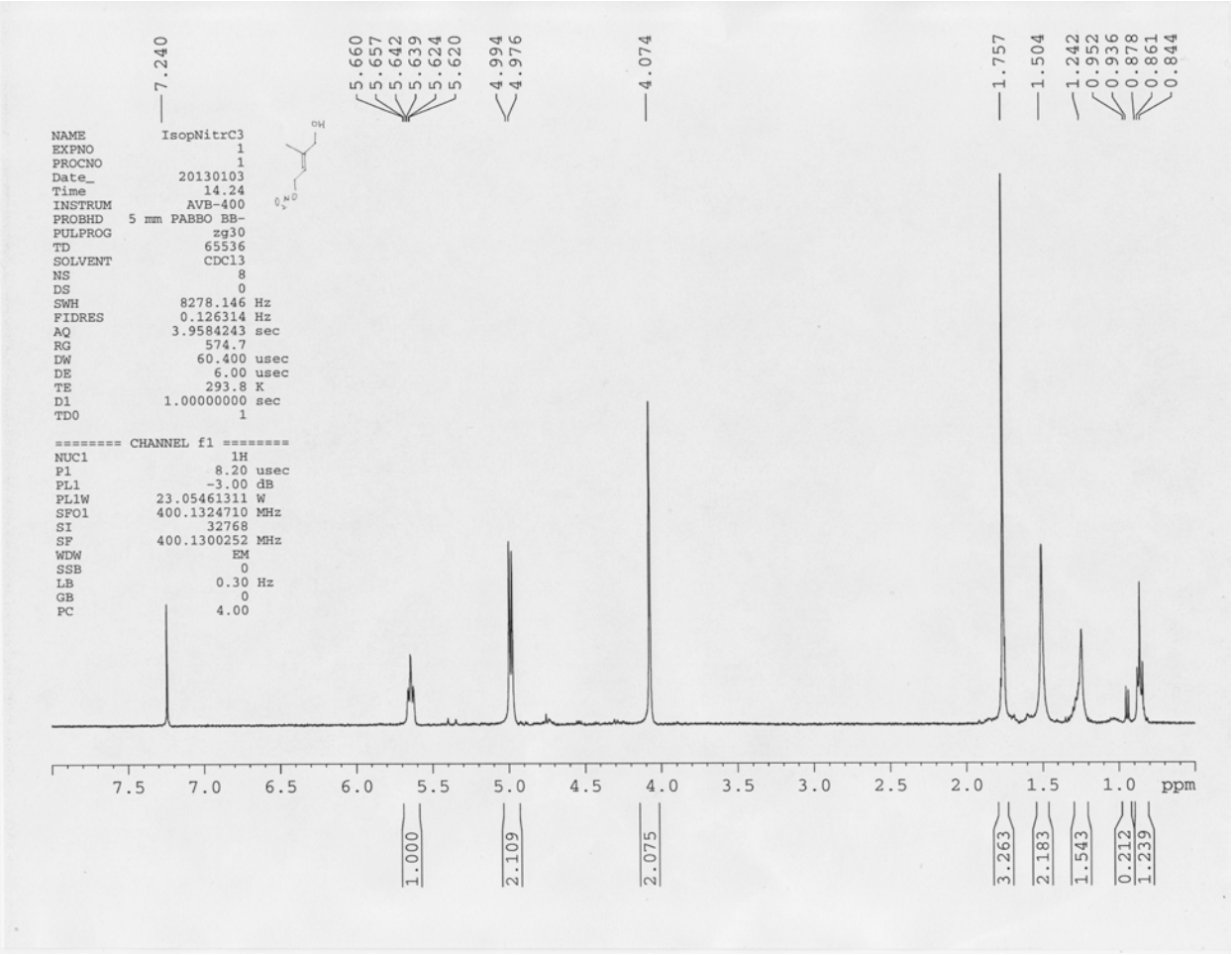
2. Geological and Planetary Sciences at California Institute of Technology, Pasadena CA 91125

3. Department of Earth and Planetary Science at University of California, Berkeley CA 94709

*(626)-395-8655; crounjd@caltech.edu; **(510)-642-2735; rccohen@berkeley.edu

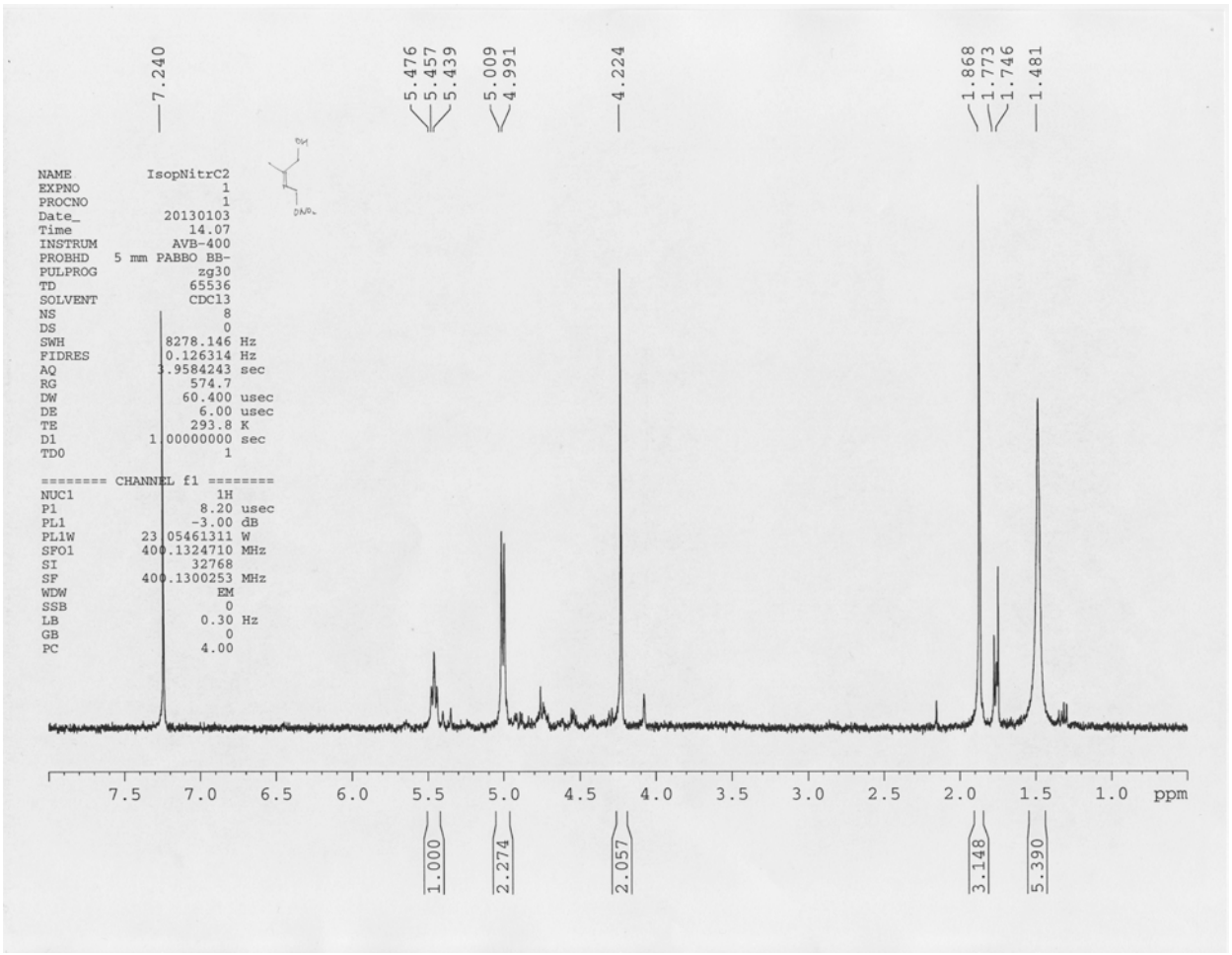
A1. NMR assignment

trans-δ-1,4 hydroxy nitrate



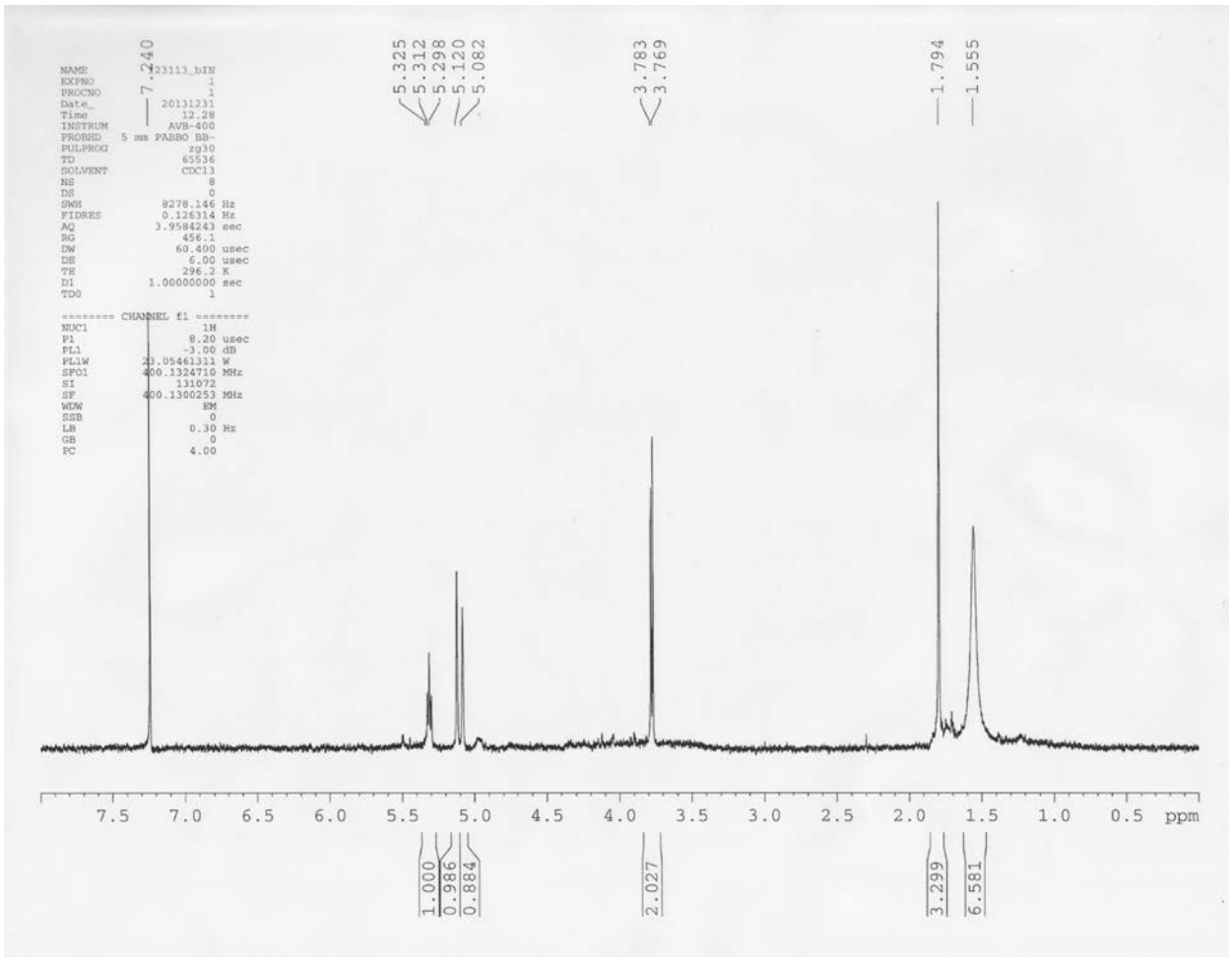
NMR spectrum of purified sample of *trans*-δ-1,4 hydroxy nitrate was measured with a Bruker 400MHz instrument in $CDCl_3$ (Sigma Aldrich, 100% D). Hydrogen on C3 is shown as a triplet centering at 5.640 ppm with coupling constant of 7.2 Hz to the hydrogen on C4 at 4.985 ppm. Hydrogen on carbon 1 and the methyl group are observed as singlet, at 4.074 and 1.757 ppm, respectively. Other peaks upfield from 1.5 ppm are residual solvent peaks such as hexane and water.

cis-δ-1,4 hydroxy nitrate



Measured under the same condition as the *trans*-δ isomer. Similar peak assignment but slight difference in chemical shift of hydrogens on C3 and C4, due to relative position with respect to the methyl group.

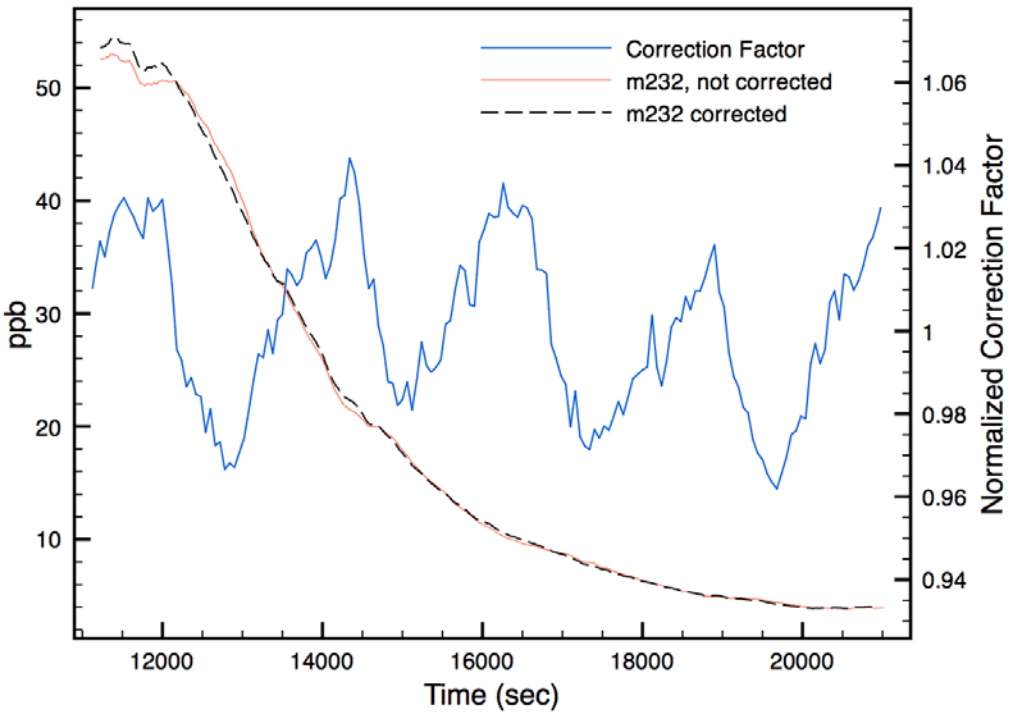
β-4,3 hydroxy nitrate



Purified β-4,3 sample after HPLC separation. The 2 singlets at 5.120 and 5.082 ppm locations are the 2 distinct hydrogens at the end of double bond. The triplet at 5.312 ppm couples to the doublet centered at 3.776 ppm with a coupling constant of 5.2 Hz, corresponding to the single hydrogen on the nitrooxy carbon and the 2 equivalent hydrogens on the hydroxy carbon. The methyl group hydrogen appears as a singlet at 1.794 ppm. The peak at 1.555 ppm is due to water. Hydrogen on the OH group is broad.

A2. Wiggle Reduction for CIMS Signal

It may be observed that the CIMS signal has certain fluctuation during the decay. Such fluctuation was thought to relate to temperature of the analog-to-digital conversion board currently being used. The temperature fluctuation on the ADC board affects the counting of the ions with a fixed pre-set discrimination threshold. Overall the temperature fluctuation gives a signal variation of approximately 6%, and may be corrected by observing that similar fluctuation is present for the total ion counts. A long running average (3600 sec) is applied to the total normalized CIMS ion signal to obtain the baseline of the correction. The correction factor is then calculated by dividing the 1 Hz CIMS total ion signal to the long-averaged value. The resulting correction factor is a time series that has the same fluctuation as the signal, but with a normalized value centering at unity. By applying the correction as a multiplicative factor, a smoother decay is obtained, as shown in figure below.



A3. Possible Interferences and Minor Reactions

In determining rate constants using relative method, interferences arise when more than one oxidant contribute to the consumption of the intended reactant and reference compounds. Under our OH experimental conditions, other possible oxidants are O_3, HO_2, RO_2 and $O(^3P)$. Ozone reaction with propene and hydroxy nitrates are much slower than OH reaction, with a rate constant around 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1}. With the measured O_3 concentration, we estimate the contribution to be less than 4%, well under our uncertainty. For HO_2, due to the excess H_2O_2 and NO in our system, the ratio of HO_2 over OH is generally around 5. Since HO_2 reaction with alkene is more than 6 orders of magnitude slower[1] than OH, the HO_2 direct contribution should be negligible. The rate constant of reaction between alkene and alkylperoxy radicals are expected to be slow[2], likely less than 1×10^{-16} cm^3 $molecule^{-1}$ s^{-1} and should not be able to compete under 100 ppbv of NO. Lastly, $O(^3P)$ is formed under UV irradiation of accumulated NO_2 in our chamber, and has been shown to react with alkene by addition reaction to yield oxirane[3] or, through hydrogen shift, ketones. Direct observation of the corresponding mass at m/z = 248 has been observed, with a tentative yield of 1.3% assuming the same sensitivity as *trans*-δ-1,4 hydroxy nitrate. Note that both oxirane and the isomerized ketones have the same mass. Assuming $O(^3P)$ reaction with hydroxy nitrate yields near 100% m/z = 248, this corresponds to an additional loss to our reactant of 1.3%. Using box model simulation with measured UV spectrum from the light banks and absorption cross section data, we estimate the fraction of reactant reacted with $O(^3P)$ to be of 0.6% using a rate constant of 3.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Paulson et al., 1995[4]), both considered to be insignificant.

Potential mass interferences from oxidation products other than ones originating from hydroxy nitrate exists and can affect estimation for product yield. Hydroxy acetone, a direct product from δ hydroxy nitrates monitored at m/z = 159 can also be formed from a minor channel in OH oxidation of propene from the corresponding β-hydroxy alkoxy radical reaction with O_2. Under our experimental condition the yield is estimated to be 1.4%. For δ hydroxy nitrate experiments the amount of nitrate reacted is very similar to the amount propene reacted, hence the net contribution of m/z = 159 from propene is only around 3%. Photolysis of some of the carbonyl compounds formed has also been considered, given the availability of literature data and we have found that the loss is too slow to have significant modification to our observed products. Due to the limited photolysis data for functionalized organic nitrates, we use nitrooxy acetone[5] as a surrogate for ethanal nitrate (m/z = 190) and methyl vinyl ketone nitrate and methacrolein nitrate (m/z = 234) and obtained a photolysis lifetime of ~48 hours from our light bank emission spectra, much longer than our typical experiment running time of ~2 hours.

A4. Parameterization for RO_2 + RO_2 Reactions

In order to achieve a reasonable representation of RO_2+RO_2 chemistry, 2 collective species are introduced, designated as (t)RO_2 and (p,s)RO_2 standing for the collective concentration of tertiary and non-tertiary peroxy radicals, respectively. The reason for such distinction is to account for the availability of α-hydrogen when proceeding through the alcohol and carbonyl forming channel of RO_2+RO_2 reactions. In cases when both RO_2 radicals are tertiary, this channel will be prohibited and an enhancement in alkoxy radical forming channel is expected. Alternatively when a tertiary RO_2 reacts with a primary or secondary RO_2, the tertiary RO_2 can only transform into the associated alcohol while the non-tertiary counterpart forms a carbonyl. Considerations for this functional group dependence and channel suppression are incorporated in our parameterizations. The collective species are not "consumed" when propagating the master equation, as equations 7~10 are formulated in such a manner that the product stoichiometry corresponds to the consumption of one $ISOPOO_x$ molecule only (not one $ISOPOO_x$ and one (x)RO_2). The products from all other RO_2 partner are calculated when iterating through all the RO_2 species. Note that when calculating (t)RO_2 and (p,s)RO_2 from lumped RO_2 species an estimation of the tertiary fraction of the lumped species may be necessary. For example, under the criteria of mass balance, $ISOPNOO_\delta$ should be considered as consisting of 0.82 (t)RO_2 and 0.18 (s,p)RO_2, while $ISOPNOO_\beta$ contains 0.36 (t)RO_2 and 0.64 (s,p)RO_2. Values for (t)RO_2 and (s,p)RO_2 are refreshed in each simulation step to reflect the current RO_2 concentration.

	Reactions			k (298K) cm^3 $molecule^{-1}$ s^{-1}
1	$ISOPNOO_\delta$ + (t)RO_2	→	0.76 HO_2 + 0.06 ROOR + 0.13 R=O + 0.1 MVKN + 0.01 MACRN + 0.36 PROPNN + 0.3 ETHLN + 0.3 HACET + 0.36 GLYC + 0.11 HCHO	5×10^{-15}†
2	$ISOPNOO_\delta$ + (p,s)RO_2	→	0.28 HO_2 + 0.02 ROOR + 0.06 R=O + 0.62 C5THN + 0.03 MVKN + 0.01 MACRN + 0.12 PROPNN + 0.11 ETHLN + 0.11 HACET + 0.12 GLYC + 0.04 HCHO	6.7×10^{-13}†
3	$ISOPNOO_\beta$ + (t)RO_2	→	0.06 NO_2 + 0.44 HO_2 + 0.04 ROOR + 0.44 R=O + 0.28 MVKN + 0.16 MACRN + 0.06 HACET + 0.06 GLYC + 0.44 HCHO	4×10^{-13}†
4	$ISOPNOO_\beta$ + (p,s)RO_2	→	0.03 NO_2 + 0.25 HO_2 + 0.02 ROOR + 0.22 R=O + 0.46 C5THN + 0.09 MVKN + 0.16 MACRN + 0.03 HACET + 0.03 GLYC + 0.25 HCHO	8×10^{-13}†

† Estimated using the rates from Jenkin and Hayman (1995)[6].
ROOR = Organic peroxide, C5THN = C5 tri-hydroxy nitrate.

References

1. Lloyd, A. C., Evaluated and Estimated Kinetic Data for Gas Phase Reactions of Hydroperoxyl Radical. *Int. J. Chem. Kinet.* **1974**, *6*, 169-228.
2. Nikisha, L. V.; Moshkina, R. I.; Polyak, S. S.; Vedeneev, V. I., Reactions of Methyl Peroxide Radicals with Ethylene. *Kinet. Catal.* **1981**, *22*, 858-862.
3. Atkinson, R., Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds .1. Alkanes and Alkenes. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215-290.
4. Paulson, S. E.; Orlando, J. J.; Tyndall, G. S.; Calvert, J. G., Rate Coefficients for the Reactions of O(P-3) with Selected Biogenic Hydrocarbons. *Int. J. Chem. Kinet.* **1995**, *27*, 997-1008.
5. Roberts, J. M.; Fajer, R. W., UV Absorption Cross-Sections of Organic Nitrates of Potential Atmospheric Importance and Estimation of Atmospheric Lifetimes. *Environ. Sci. Technol.* **1989**, *23*, 945-951.
6. Jenkin, M. E.; Hayman, G. D., Kinetics of Reactions of Primary, Secondary and Tertiary Beta-Hydroxy Peroxyl Radicals - Applications to Isoprene Degradation. *J. Chem. Soc. Faraday T.* **1995**, *91*, 1911-1922.